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## SOME CHARACTERISTICS OF THE DERIVATIVES OF TRICHLORMETHYLPHOSPHONIC ACID

A. Ya. Yakubovich, V. A. Ginsburg

Only the esters of trichlormethyl and trichlormethylphenylphosphonic acids prepared by Kamay (1) with carbon tetrachloride by Arbuzov's reaction are well known. While studying the properties of chlormethyldichlorphosphine (2), we found another method of synthesizing trichlorphosphine derivatives, which made available various compounds of this type.

Chlormethyldichlorphosphine forms, through the action of a molar quantity of chlorine, the normal tetrachloride ClCH2PCl4. With an excess of chlorine, it halogenates easily and quantitatively further in the methyl radical as follows:

Bromination takes place analogously but slower. Dichlormethyl-, trichlormethyl-, and (in bromination) chlorbrommethyltetrahalides of phosphorus thus obtained were used for further conversions. Upon hydrolysis, CECl\_PCl\_1 and CECl\_BrPCl\_BrpCreadil; form the corresponding acids. Phosphorus trichlormethyltetra-chloride dissolves very slowly in cold water or 0.5N alkali. By dissolving CCl\_3-PCl\_1 or CCl\_3POCl\_2 in hot water, the crystalline monobasic acid of the composition CCl\_3PO(Cl)OH is quantitatively formed, which is completely stable to hydrolysis. With aniline, this compound forms CCl\_3PO(Cl)OH·C\_6H\_5NH\_2. In an excess of a damp ether solution of diazoethane, either the acid or the neutral ethyl ester of trichlormethylphosphonic acid is formed depending on the composition of the mixture:

$$CCl_3PO(Cl)OH \xrightarrow{H_2O} CCl_3PO(OC_2H_5)OH + C_2H_5Cl + 2N_2$$

 $\text{CCl}_3\text{PO}(\text{CC}_2\text{H}_5)\text{OH} \xrightarrow{\text{CH}_3\text{CHN}_2} \text{CCl}_3\text{PO}(\text{CC}_2\text{H}_5)_2 + \text{N}_2$ 

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This neutral ester can be obtained by the reaction  $CCl_3PCl_4 + 4C_2H_5ONO \rightarrow CCl_3PO(OC_2H_5)_2 + 4NOC1 + (C_2H_5)_2O$ .

The diethyl ester was originally described by Kamay (1).

With the purpose of getting trichlorphosphonic acid, the saponification of its esters under various conditions was studied. It developed that in an alkaline medium (barium hydroxide) the diethyl ester of trichlormethylphosphonic acid undergoes splitting at the C-P bond with the formation of chloroform:

$$\frac{\text{CCl}_3\text{PO(OR)}_2}{\text{PO(OR)}_2} = \frac{\frac{\text{H}_2\text{O}}{\text{Ba}(\text{OH})_2}}{\text{CCl}_3\text{H}} + \frac{\text{H}_3\text{PO}_4}{\text{H}_3\text{PO}_4} + \frac{\text{2c}_2\text{H}_5\text{OH}}{\text{OH}_3\text{PO(OR)}}$$

Saponification of the ester in cold 15% HCl results in the formation of the above-described acid ester  $CCl_3PO(OC_2H_5)OH$ , even though the saponification may have been carried out for a very long time (2-3 months).

Free trichlormethylphosphonic acid (in the monohydrate form) forms in practically quantitative yields during the saponification of its esters in 15% HCl at  $140-150^\circ$  for 3-4 hr.

According to Kamay's data, the initial acid cannot be obtained by saponification of the esters of trichlormethylphosphonic acids. The reaction allegedly is accompanied by a full decomposition of the ester and the formation of phosphoric acid. These assertions, according to our data, are erroneous.

Trichlormethylphosphonec acid is dibasic. Silver nitrate precipitates its disilver salt, which dissolves with difficulty in water. This salt decomposes explosively under light heating. On treating the acid with diazoaliphatic compounds, the corresponding esters are obtained.

In accordance with Kamay's data, trichlormethylphosphonates react with aniline as follows:

$$cc1_3PO(OR)_2 + HNHC_6H_5 \rightarrow CC1_3H + C_6H_5NHPO(OR)_2$$

We were unable to substantiate this. The methyl and ethyl esters of trichlormethylphosphonic stids behaved alike when heated with aniline in boiling toluene, forming aniline saids of acid esters of trichlormethylphosphonic acid.

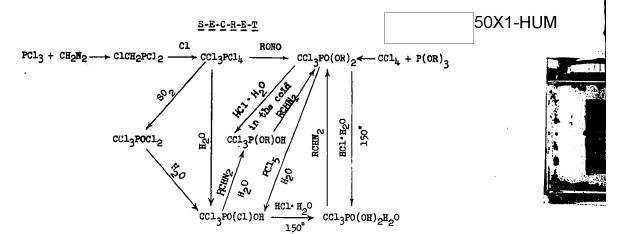
Thus the reaction seems to consist of the alkylation of aniline as follows;

$${}^{\text{CC1PO}(gR)_2} + {}^{\text{CC1}_5\text{NH}_2} + {}^{\text{CC1}_3\text{PO}(GR)\text{OHC}_6\text{H}_5\text{NH}_2} + {}^{\text{C}_6\text{H}_5\text{NHR}}$$

Experimental mata seem to refute modd and Atherton's scheme for this reaction (3).

In order to establish relationship between CCl<sub>3</sub>PO(OH)<sub>2</sub> and CCl<sub>3</sub>PO(Cl)OH, the conditions of their mutual transformation were found. Thus trichlor-methylphosphonic acid monochloride, after being heated in a sealed tube with HCl, becomes trichlormethylphosphonic acid. Treating the acid CCl<sub>3</sub>PO(OH)<sub>2</sub> with an excess of PCl<sub>5</sub> or SCCl<sub>3</sub>PO(OR)<sub>2</sub> with the expected acid chloride. Heating the ester CCl<sub>3</sub>PO(OR)<sub>2</sub> with the corresponding amount of PCl<sub>5</sub> at 1500 changes the ester into acid /di/ chloride, which, after hydrolysis, yields trichlormethylphosphonic acid monochloride. Some of the reactions of trichlormethyl derivatives of phosphorus can be graphically illustrated as follows:





From other trichlormethyl derivatives of phosphorus we obtained derivatives of tri (trichlormethyl) phosphine. Thus, by treating tri (chlormethyl) phosphinoxide with phosphorus pentachloride we obtained the perchloride (CCl<sub>3</sub>)<sub>3</sub>PCl<sub>2</sub>. This substance, after boiling in alkali hydroxide, splits off at least one atom of chlorine and becomes the oxychloride (CCl<sub>3</sub>)<sub>3</sub>P(Cl)OH. Treatment of the latter in solution with aniline removes HCl:

$$(CCl_3)_3 P_{OH} \xrightarrow{C_6 H_5 NH_2} (CCl_3) P = 0$$

Thus, introduction of the trichlormethyl group at the phosphorus atom results in a number of peculiarities in the behavior of this type of organophosphorus compounds. The most important ones are:

- 1. Sharp decrease in the reactive capacity of the chlorine atom attached to the phosphorus in respect to hydrolysis and ammonolysis.
- 2. Appearance of a specific reactive capacity of the C P bond with respect to alkalies, as illustrated by the fact that the CCl<sub>3</sub> P group behaves like the CCl<sub>3</sub> C or CCl<sub>3</sub> Si groups, which in many cases are capable of splitting off chloroform easily under the action of a strong base.
- 3. The introduction of halogenin, to the methyl group intensifies the acidic properties, so that trichlormethylphosphonic acid is free to form the dianiline salt.
- 4. The presence of the CC13 group next to the phosphorus atom contributes to the stability of the unusual  $P_{C1}^{OH}$  group.

The listed features point to a similarity in chemical behavior of trichlor-methylphosphonic derivatives and compounds of the type of Boyd's acid chloride(4, 5).

Table 1. Properties of the Obtained Organophosphorus Compounds

Compound	Melting Pt	<u>Bp</u>	Denr 'ty	20 20
CHCl <sup>S</sup> PCl <sup>†</sup>	Decomposes			
CHC1 <sup>5</sup> bo(OH) <sup>5</sup>	54			
снствъъьо(он) <sup>5</sup> .5с <sup>6</sup> н <sup>2</sup> ин <sup>5</sup>	180-185 decomposes			,

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<u>S-E-C-R-E-T</u>								
Compound	Velting Pt	Вр	Density	n <sup>20</sup>				
CC13PC14	125, decompose	s						
cc1 <sup>3</sup> boc1 <sup>5</sup>	155							
CC13PO(OCH3)2*	37	109-109.5/9	m d <sub>0</sub> = 1.483					
CC13F0(0C2H5)2**		122-123/13	$d_0^{14} = 1.3710$	1.4620				
CC13b0(0H)5. H <sup>5</sup> 0	87		. 40 - 1.3/10	1.4620				
сст <sup>3</sup> ьо(он) <sup>5</sup> .с <sup>ен<sup>2</sup>ин<sup>5</sup></sup>	Above 220		\					
CC13PO(OH)2.2C6H5NH2	Above 220							
CC13PO(OAg)2	Explodes							
CC13PO(CI)NHC6H5	113							
CC13PO(NHC6H5)2	172							
CC13PO(CC2H5) OH-								
· C?H2NH5	176, decomposes							
сс13ьо(осн3)он.с <sup>6н2</sup> ин <sup>5</sup>	172, decomposes							
CC13PO(C1)OH	79							
CC13bo(c1)OH.CPH2NH5.	191, decomposes							
(CC1 <sub>3</sub> ) <sub>3</sub> PC1 <sub>2</sub>	190, decomposes							
(cc13)3b(c1)OH	203	<b>-</b>						
(CC1 <sub>3</sub> ) <sub>3</sub> P = 0	53							
	- <b></b>		j					

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\*Described by Kamay as a liquid boiling at  $121^{\circ}/12$  mm;  $d_0^{15}$  = 1.4594;  $n_D^{14}$  = 1.4580

\*\*Described by Kamay as boiling at 122-123°/12 mm;  $d_0^{14} = 1.3664$ ;  $n_D^{14} = 1.4585$ 

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